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The transfer of atoms, ions and molecular groups

in solution. Part 1--Models and limits

by

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The theory of the activated complex, as formulated by Marcus, is applied to the transfer in condensed phases of atoms, ions and molecular groups. Particular attention is given to reactions which take place in the diabatic limit. A Born-Oppenheimer-Holstein separation is developed in order to separate the degrees of freedom of the reactive subsystem from those of the environment; perturbations which can drive the reaction in the diabatic limit are

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identified. An analysis of a simple system is carried out. The system is two-dimensional and consists of a lithium cation which migrates (via activation) from one site of solvation to another. The development of the paper and the exmaination of the simple, ideal system reveal the following. First, diabatic transfers can occur only over short distances for the tunnelling (vibrational overlap guarantees this result). Secondly, if the reaction follows a completely adiabatic path, the migrating species will occupy a position of stable mechanical equilibrium in the transition state. Thirdly, if the reaction is diabatic, the migrating species adiabatically follows a path to the initial state for the tunnel transfer; the work of creating the initial state enters the expression for the energy of activation, as is well known. Finally, it is possible, in terms of the specific development of the paper, to formulate either an optimal or Monte Carlo method for determining the configuration and energy of the transition state. An optimal method for investigating the transition state can use a minimum number of molecules of solvent. This particular development draws a close parallel to the work of Glyde on the self-diffusion of solid argon.

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The Transfer of Atoms, Ions and Molecular Groups

in Solution. I. Models and Limits

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Abstract

The theory of the activated complex, as formulated by Marcus, is applied to atomic, ionic, and molecular group transfers which take place in condensed phases. Particular attention is given to reactions which take place in the diabatic limit. A Born-Oppenheimer-Holstein separation is developed in order to separate the degrees of freedom of the reactive subsystem from those of the environment; perturbations which can drive the reaction in the diabatic limit are identified. An analysis of a simple system is carried out. The system is two-dimensional and consists of a lithium cation which migrates (*via* activation) from one site of solvation to another. The development of the paper and the examination of the simple, ideal system reveal the following. Diabatic transfers can occur only over short distances for the tunnelling (vibrational overlap guarantees this result). If the reaction follows a completely adiabatic path, the migrating species will occupy a position of *stable* mechanical equilibrium in the transition state. If the reaction is diabatic, the migrating species adiabatically follows a path to the initial state for the tunnel-transfer; the work of creating the initial state enters the expression for the energy of activation, as is well known. Finally, it is possible, in terms of the specific development of the paper, to formulate either an optimal or Monte Carlo method for determining the configuration and energy of the transition state. An optimal method for investigating the transition state can use a minimum number of molecules of solvent. This particular development draws a close parallel to the work of Glyde on the self-diffusion of solid argon.

Introduction

It is our general purpose in this and succeeding papers to explore the application of the activated complex theory of reaction rates to a number of systems which involve the transfer in solution of atoms, ions, or molecular groups. These transfers may be associated with species-transfer (diffusion), with intermolecular reactions, or with intramolecular rearrangements. For many of these *heavy-centre* transfers there is also an accompanying (intra- or intermolecular) electron transfer; thus, certain forms of oxidation/reduction reactions can be included in the general scheme. A goal of this work is to attempt to formulate a computational theory for this class of reactions which should yield accurate values for the rate constants for arbitrary, real systems. Part of the scope of this work, therefore, can be described as algorithmic, building strategies to use to compute rate constants for particular, well-defined classes of model systems. And, part of the scope of this work necessarily is to define these models and to specify their limits of applicability.

The process of developing a practical, computational theory of heavy-centre transfer begins with the activated complex theory as cast in its most general form by Marcus.[1] Some time ago, we also showed[2] that in the semiclassical limit, the activated complex theory of diabatic (electron-transfer) reactions evolves naturally from a quantum mechanical formalism. This formalism applies as well to the heavy-centre transfer. Thus, within one theoretical framework it is possible to consider a variety of diverse types of reaction for two fundamental limits: diabatic and adiabatic.

Much of the appeal of the electron-transfer theory is in its obvious modelling and in its equally obvious (with hindsight) treatment in terms of the fluctuations of the polar environment.[3-5] An analogous modelling for atom-, ion-, and molecular group-transfer is also possible; although, in order to do so it is necessary to return to the consideration of the general form of the theory of the activated complex. This we shall do. However, even before considering the application of the theoretical techniques, it is necessary to consider the reacting system, to break it down into its definable subsystems, and to identify the forms of the interactions which link one subsystem with another. As part of the goal of this work is to develop a practical theory of heavy-centre transfer, we plan to explore this part of the modelling process in terms of particular assumptions about the nature of the systems and in terms of particular forms of the effective potential energy functions. In this initial treatment, therefore, we deal with ideal model systems and make no immediate claim of accuracy for the calculated values of the rate constants. Indeed, as an example we consider ionic diffusion in a hypothetical two-dimensional fluid. We are concerned at this time with establishing the reasonableness of the results for the models as they are defined. As the work evolves, analyses of real systems will be considered. For the present, it is our intention to establish the techniques in general and to sketch the application of these techniques to certain simplified systems.

Modelling: basic notions

Whether one intends to consider the transfer of an atom, an ion, or a molecular group, certain general and simple ideas about the character of the reactive system seem to be naturally self-evident. In particular, two distinct limits for the transfer can be defined.

In the first limit, the immediate environment of the transferring species is *effectively rigid*; for the heavy-centre transfer, this is analogous to the outer-sphere electron-transfer. As we shall show, this limit imposes the restriction that the actual distance for the transfer must be relatively short. The shortness of the distance is determined by the requirement that the vibrational overlap factors must not be vanishingly small. Finally, interactions couple fluctuations of an effectively continuous, remote environment with the migrating species. Thus, by means of these couplings to the fluctuations of the environment the transfer is activated.

There is a wealth of chemical lore to support this view of the reacting subsystem. The S_N2 mechanism for substitution in organic chemistry, and many counterparts in inorganic chemistry as well[6] attests to the soundness of the argument that (to begin with) the rearrangement of atoms which leads from an initial to a final configuration ought to be as small as possible.

The second limit applies to transfers over large molecular distances. Such transfers are observed, and they defy the limit imposed in the first case of an effectively outer-sphere transfer.

For long-ranged transfers, the direct vibrational overlap factors (which, as mentioned, must not vanish in the first limit) essentially vanish for the distances which are involved. Activation in this second limit can occur only by means of the extensive, cooperative fluctuations of the environment. The fluctuations must cause a substantial readjustment of the reactive system.

It is necessary to note, however, that it is possible for a reaction to involve a large-scale rearrangement of the reactive system and still be characterized by the first limit. In each of these limits, the energy of reorganization of the reactive system and its environment enters as a dominant term in the energy of activation. If the energy necessary to prepare the reactive system in a state from which transfer ultimate takes place enters as a definable work term, then the reaction is characterized by the first limit. The exact manner by which this work term enters is defined by the theory of the activated complex, and is reviewed in a later section in this paper.

An important distinction between the first and second limits is the fact that in the first limit heavy-centre tunnelling can be the dominant route for the transfer. Although tunnelling is definable in the second limit, as indicated, the vibrational overlap factors are vanishingly small, and tunnelling probably figures minimally in any mechanism at the molecular level. Thus, the first limit for a heavy-centre transfer is most likely to be a diabatic limit for the transfer (although, it is possible to define an adiabatic limit in this case). The second limit, which applies to long-distance transfers, is most certainly an adiabatic limit.

There is evidence that for some systems, and in particular for some solvated cations, definite structures of solvation persist for sufficient lengths of time for one to be able to define *majority* *configurations* within which the ions oscillate. The far infrared-active spectra of the simpler solvated cations of the elements of Groups I & II seem to support this view.[7-10] It is reasonable, therefore, to assume that the notion of a majority structure of solvent ought to apply to a broad class of systems. This notion will be used here in order to define part of the reactive subsystem, and to mark its boundaries with the remainder of the system.

In the following sections, we develop a quantitative analysis of the two limits for the types of transfer which were defined above. With the use of the activated complex theory, it is possible to see clearly just how the limits apply in practice.

Modelling: reactive subsystem

The reactive subsystem is defined as the smallest number of species (solute and solvent) which is required to construct a structure within which the transfer or transformation is un-ambiguously described. Thus, the reactive subsystem depends upon discrete structures of solvent to the extent that these discrete structures are needed to define a specific path for the transfer or transformation.

For example, in order to describe the diffusion of an atom, ion or molecule in solution, it may be sufficient merely to con-sider only the primary shell of solvent and sufficient numbers of secondary solvent as are required to define vacancies into which the species can migrate. Such a structure is defined in isolation;

the elementary mechanics of the migration of the solute in the structure can be considered. Finally, the subsystem is allowed to interact with the remainder of the solvent in order to study the role of fluctuations in driving the mechanical transformations which have been defined for the simple, primary system. On the other hand, for a typical intramolecular transformation, as for example a *cis-trans* isomerization, it is usually sufficient to consider the isolated molecule as the primary form of the reactive subsystem.

When, for either of these examples, it becomes necessary to add molecules of solvent to the primary structure because the interaction between the solvent and solute is strong, it is a simple matter to expand the primary structure to include these strongly interacting species. Eventually, one assumes for regular systems, the interaction between the solvent at the boundary of the primary structure and the remainder of the system approaches the limit of a regular solvent-solvent interaction. A boundary may have to be extended (for some cases) to considerable distances in order to realize the onset of equal solvent-solvent interactions. It is an assumption of this work that such a boundary can be found.

Finally, we shall assume that for the solution phase, a straight-line trajectory from the initial to the final state is reasonable. This is certainly not generally the case for reactions in the gas phase. A straight-line trajectory is reasonable for the solution phase simply because most transfers take place over relatively short distances; the distances are certainly short in comparison with the gas phase where curved trajectories may be mandatory.

This assumption suggests a simple algorithm to use to determine

the reaction coordinate. Assume a random distribution of solvent
has been generated in the vicinity of the transferring species.
If a vector can be drawn from the initial location of the
migrating solute (or part of the solute, *viz.*, a molecular group)
to a vacancy *without requiring the displacement of solvent*, then
that vector defines a possible path. The vector associated with
the *most likely path* is that vector which takes the migrating species over
the *lowest* potential energy-barrier (again without the distortion
of the solvent).

Once the most likely path has been found, the reactive subsystem
is placed in contact with the remainder of the system. The
migrating species is placed at the physical location of the
maximum of the energy-barrier. With the transfer-species frozen
at that position, the system is allowed to relax to a configuration
which yields the lowest energy; this is the energy of the transition
state. The entire process is made quantitatively explicit in
later sections. It is in fact the process which has been used
by Marcus[1] and by Glyde.[11]

Modelling: environmental considerations

The environment about the reactive subsystem is perhaps the
most difficult part of the entire system to describe. For the
electron-transfer reaction, for example, it is frequently possible
to obtain reasonable agreement with experiment for some reactions
with the use of a polarizable continuum. The couplings are well-
defined, and the analysis proceeds in much the same manner as
in the polaron theory.[3-5]

The idea that a single oscillator can relax as a result of
anharmonic couplings to the remaining normal modes of a solid
has been developed for several systems. Opie[12] was the first
to argue that the coupling of an oscillator to the remaining modes
could be treated as a single oscillator coupled to a loss-field.
Opie's analysis is based in part on Senitzky's[13] theory of the
loss-field. Nitzan and Jortner[14] applied a similar form of this
analysis to the problem of the vibrational relaxation of a molecule
in a dense medium. In all of these developments, the role of the
fluctuation/dissipation theorem is evident; couplings which can
lead to the relaxation of a local oscillator also (*via* a reverse
process) can lead to the activation of excited states of the
oscillator.

The manner by which these environmental fluctuations cause a
system to populate the transition state will be treated here in
a general form. We shall argue, following Marcus[1] and Glyde,[11]
that a representation of the environment can be given simply in
terms of the potential V, the effect of which is specified, but the
form of which is left open.

Born-Oppenheimer-Holstein Separation: vibrational systems

The problem of finding an effective potential energy function for
the interaction between solvent and solvent and between solvent
and solute in solution is of long-standing, and by no means resolved.
In view of this, we treat the interactions symbolically in the
development of the expressions for the rate constant. Once the
formula for the rate constant has been derived, it will be
possible to see how to use any particular choice of effective

potential energy function in the subsequent numerical evaluation.

We assume pair-wise solute-solvent interactions. Thus, the potential energy function for the motion of the transfer-species along the transfer-axis (the z-axis) of the reactive subsystem is

$$V(z) = \sum_{i=1}^{N} V_i(z) \qquad (1)$$

where $V_i(z)$ is a symmetry-adapted expansion in a Taylor series for an individual interaction between the solute and solvent (or atom within the solvent). There are N species outside of the solute which contribute to the summation.

The symmetry-adapted Taylor series for an arbitrary potential energy function $V(r)$ is

$$V(r+R) = \sum_{n=0}^{\infty} \frac{r_<^n}{n!} \sum_l \left[A_{nl} P_l(\hat{r}\cdot\hat{R}) \sum_{q=0}^{l} \frac{(-1)^q (l+q)!}{(l-q)!(2q)!} r_>^{-q} \left(\frac{n-q}{r_>}\right) \right.$$
$$\left. + \frac{d}{dr_>}\right] \left(\frac{d}{dr_>}\right)^{n-q-1} V(r_>). \qquad (2)$$

The derivation of this particular form is based on the use of specific forms which are reported elsewhere.[9,15] The derivation is outlined in an appendix. In the expression above, A_{nl} is

$$A_{nl} = \frac{(2l+1)n!(n-l+1)!!}{(n-l)!!(n+l+1)!!} \quad \text{for } l \leq n \text{ and } n-l \text{ even}$$

$$= 0 \quad \text{for } l > n \text{ and } n-l \text{ odd.} \qquad (3)$$

The general argument of V, $r+R$, is the vector drawn from the solvent (or atom of solvent) to the instantaneous location of

the solute. Note, that in the formulation as it now develops, this vector is drawn to the centre-of-gravity of the solute, as we are considering the migration of the entire species. The vector R locates a particular point for the expansion in terms of the position of the solvent. The vector r represents the displacement of the solute from the point of expansion. The quantity $r_{<(>)}$ is the lesser (greater) of r and R. The $P_n(x)$ are Legendre polynomials,[16] the arguments of which in eqn (2) are $\hat{r}\cdot\hat{R} = \cos\theta$ with θ the angle between r and R. The quantities $\hat{r}$ and $\hat{R}$ are the unit vectors which are associated with r and R.

The Legendre polynomial in eqn (2) can be expressed in terms of the spherical harmonic functions which are referred to the origins of the vectors r and R:[17]

$$P_l(\hat{r}\cdot\hat{R}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y^*_{lm}(\hat{r}) Y_{lm}(\hat{R}); \qquad (4)$$

and Y_{lm} is the spherical harmonic function. As the z-axis is the axis for tunnelling.

$$P_l(\hat{r}\cdot\hat{R}) = P_l(\cos\theta_R) \qquad (5)$$

in which θ_R specifies the angle which the vector R makes with reference to the z-axis. In eqn (2) we now replace $r_{<(>)}$ as the lesser (greater) of r and R with $z_{<(>)}$ as the lesser (greater) of z and R. The particular application of the expansion is illustrated later with the use of a specific, simple example: the tunnelling of a simple, spherical ion from one structure of solvent to another.

The zeroth-order *vibrationally adiabatic* Hamiltonian operator for the transfer-species in its reactive subsystem is given by

$$H_t = T + V \qquad (6)$$

in which T is the kinetic energy operator for the transfer species and V is the potential energy operator as expressed by eqn (1) and developed with eqn (2). In other words, V is V(z), the potential energy operator for the motion of the transfer-species along the transfer-axis.

In the following, we assume that the harmonic oscillator basis functions can be used in order to develop the Born-Oppenheimer-Holstein[18,19] separation of the local modes of the transfer-species from the remainder of the modes of the system. We retain the complete expansion of V for the motion of the transfer-species along the z-axis, not merely a truncation of it at the harmonic limit.

For the initial state, in which the transfer-species is located in a state of mechanical equilibrium at site a, we specify the Hamiltonian operator H_{0a} as

$$H_{0a} = p^2/2m + \tfrac{1}{2}k_a z^2 \qquad (7)$$

for which k_a is an effective vibrational force constant; this force constant corresponds to the observed frequency of oscillation of the transfer-species at a. This quantity also can be used as a variational quantity, as will be evident. A similar term applies to the transfer-species at the location b. Thus, H_t can

be written equivalently as

$$H_t = p^2/2m + \tfrac{1}{2}k_a z_a^2 + V(x) - \tfrac{1}{2}k_a z_a^2$$
$$= H_{0a} + V(z) - \tfrac{1}{2}k_a z_a^2$$
$$= H_{0b} + V(z) - \tfrac{1}{2}k_b z_b^2. \qquad (8)$$

The operators $V(z) - \tfrac{1}{2}k_{a(b)}z_{a(b)}^2$ act as perturbations on the zeroth-order harmonic oscillator states. The eigenfunctions of the local harmonic Hamiltonian operators satisfy

$$H_{0a(b)}\phi_{a(b)} = \tfrac{1}{2}\hbar\omega_{a(b)}(2n_{a(b)} + 1)\phi_{a(b)}. \qquad (9)$$

The total Hamiltonian operator for the system is

$$H = H_t + H_{env} \qquad (10)$$

and H_{env} contains kinetic and potential energy operators for all species except the transfer species. In addition, it contains all the solvent-solvent and other interactions for the reactive subsystem which were not used in the definition of V(z). The Schrödinger equation for the complete system is

$$H\psi = E\psi \qquad (11)$$

with

$$\psi = \sum_{i,\gamma} X_{i\gamma}\phi_{i\gamma}$$ (12)

In this equation, the subscript i labels the physical origin (a or b) of coordinates for the wavefunction and γ labels the vibrational state for the transfer species at the site i. With the use of eqn (12) in (11), it is possible to generate the matrix equation (13)

$$SE^0X = VX$$ (13)

in which S is the vibrational overlap matrix, E^0 is a diagonal matrix with elements

$$E^0_{i\gamma,j\delta} = (E - E^0_{i\gamma})\delta_{i,j}\delta_{\gamma,\delta}$$ (14)

The energies $E^0_{i\gamma}$ are given by eqn (9). The matrix elements of V are

$$V^j_{i\gamma,j\delta} = \langle i\gamma|V - \tfrac{1}{2}k_j z_j^2|j\delta\rangle + \langle i\gamma|H_{env}|j\delta\rangle.$$ (15)

With the use of S^{-1}, the inverse of the overlap matrix S, one finds the equation

$$HX = S^{-1}VX$$ (16)

where H is a diagonal matrix

$$H_{i\gamma,j\delta} = (E - E^0_{i\gamma} - L_{i\gamma,j\delta})\delta_{i,j}\delta_{\gamma,\delta}$$ (17)

The matrix elements $L_{i\gamma,j\delta}$ are defined by

$$L_{i\gamma,j\delta} = \sum_{k,\epsilon} S^{-1}_{i\gamma,k\epsilon}V^j_{k\epsilon,j\delta}.$$ (18)

The equation to determine any particular element of the vector X is

$$H_{i\gamma,i\gamma}X_{i\gamma} = \sum_{j,\delta}{}' L_{i\gamma,j\delta}X_{j\delta}$$ (19)

and the summation on the right hand side excludes the diagonal elements $L_{i\gamma,i\gamma}$.

The environmental vector X is determined in the adiabatic limit as a solution to the equation

$$\sum_{k,\epsilon} S^{-1}_{i\gamma,k\epsilon}(\langle k\epsilon|H_{env}|i\gamma\rangle + \langle k\epsilon|V - \tfrac{1}{2}k_i z_i^2|i\gamma\rangle)X_i$$
$$= (E - E^0_{i\gamma})X_{i\gamma}$$ (20)

As H_{env} contains kinetic and potential energy operators for all species in solution, except for the transfer-species, this equation has the usual form of the Schrödinger equation for a collection of anharmonic oscillators. One sees that in eqn (19) the terms on the right hand side act as perturbations which can drive the species-transfer ... state γ on site a to a state δ on site b.

The Born-...tein (BOH) separation,[18] as applied to the transfer of an atom, ion or molecular group, can be

regarded as an extreme form of normal mode analysis. It works adequately only for reactions which satisfy a diabatic limit for the transition. When the interactions are strong, and the transformation is adiabatic, some other form of separation of variables must be considered; Marcus[20,21] has considered this problem for the construction of potential energy surfaces. The resulting analysis may clearly differ from the BOH analysis which was considered above.

The BOH separation enables one to consider the diabatic limit. In the case for which the interaction between the reactive subsystem and the environment is strong, it is still possible for the BOH analysis to be applied. In particular, if the final (activated) transfer takes place from an initial state (which is distantly removed from a thermodynamic initial state for the system) *via* a tunnel-mechanism, then the BOH analysis can be applied to the particular reactive configuration. As is noted later in the paper in detail, a diabatic transfer can be characterized by the fact that in the transition state the transfer species *cannot* occupy a state of mechanical equilibrium with respect to the configuration of species in that state. This implies that coupling to the final state for the transfer is weak in the sense that the vibrational overlap is small.

Theory of the Activated Complex: diabatic limit

The BOH analysis defines initial and final states for the transfer of a heavy-centre (*i.e.*, any particle apart from an electron). Moreover, given well-defined initial and final states, the L-

operators define perturbations which link these states. The analysis evolves from time-dependent perturbation theory, and the results are well-known.

The transition probability for the transfer from site a to b is averaged over all possible initial states and summed over all final states; the result is written as

$$w_{ab} = \frac{2\pi}{\hbar Q} \sum_{i,f} e^{-\beta E_i} |\langle i | L_{a\gamma,b\delta} | f \rangle|^2 \delta(E_f - E_i).$$ (21)

The states $|i\rangle$ and $|f\rangle$ are associated only with the environmental degrees of freedom, and the energies E_i and E_f are Born-Oppenheimer adiabatic quantities. The summation over the initial and final states can include summation over local vibrational states of the transfer-species. The Dirac delta function $\delta(E_f-E_i)$ ensures conservation of energy for the transfer. Finally, Q is the partition function

$$Q = \sum_i e^{-\beta E_i}$$ (22)

and $\beta = 1/k_B T$ where k_B is Boltzmann's constant.

In order to manipulate this expression, we use the integral representation of the delta function to write

$$w_{ab} = \frac{1}{\hbar^2 Q} \sum_{i,f} \int_{-\infty}^{\infty} dt \langle i | L_{a\gamma,b\delta} \exp(itE_f/\hbar) | f \rangle$$
$$\times \langle f | L_{b\delta,a\gamma} \exp[-(\beta+it/\hbar)E_i] | i \rangle.$$ (23)

The operator identity $e^{i\alpha H}\psi_{t_n} = e^{i\alpha E_{n}}\phi_n$, for $H\psi_n = E_n\phi_n$, together with

the (assumed) completeness of environmental states, $\Sigma_f |f\rangle\langle f| = 1$, enable us to write eqn (23) as

$$w_{ab} = \frac{1}{\hbar^2 Q} \sum_i \int\int_{-\infty}^{\infty} dt \langle i| L_{a\gamma,b\delta} e^{i\beta H_{b\delta,b\delta} t/\hbar} e^{-(\beta+it/\hbar)H_{a\gamma,a\gamma}} \\ \times L_{b\delta,a\gamma} |i\rangle. \quad (24)$$

Now, assume the classical limit for the environmental subsystem. This implies that the commutator $[H_{a\gamma,a\gamma}, H_{b\delta,b\delta}] = 0$, and that the arguments of the exponential functions in eqn (24) can be directly combined. The kinetic energy cancels in $H_{b\delta,b\delta} - H_{a\gamma,a\gamma}$ to give $U_f - U_i$. Eqn (24) now is

$$w_{ab} = \frac{2\pi}{\hbar Q} \int\int d(P) d(R) e^{-\beta H_{a\gamma,a\gamma}} |L_{a\gamma,b\delta}(R)|^2 \delta(U_f - U_i) \quad (25)$$

in which $d(P)d(R)$ is the element of phase space. The partition function now is

$$Q = \int\int d(P) d(R) e^{-\beta H_{a\gamma,a\gamma}}. \quad (26)$$

The matrix elements $L_{a\gamma,b\delta}$ depend in general on z, the transfer-axis. The distance over which the species transfers from site a to site b depends on one coordinate R; this coordinate is normal to the hypersurface for the reaction and is a measure of the separation between sites a and b. The quantity

$$\frac{2\pi}{\hbar} |L_{a\gamma,b\delta}|^2 \delta(U)$$

has a dimension of frequency. We assume that it is (effectively) independent of momenta, especially the momentum conjugate to z, the transfer-axis. Then,

$$w_{ab} = \frac{2\pi}{\hbar q} \int d(R) e^{-\beta U_i} |L_{a\gamma,b\delta}|^2 \delta(U_f - U_i) \quad (27)$$

where q is the configurational integral

$$q = \int d(R) e^{-\beta U_i}. \quad (28)$$

The remaining integration in eqn (26) which involves the delta function can be carried out as follows. The relationship

$$\delta(f(R)) = (\partial f/\partial R)^{-1} \delta(R) \quad (29)$$

can be used to transform $\delta(U_f - U_i)$ from an implicit dependence on R to an explicit one. The integration will involve only the coordinate z (on the transfer-axis). At some point on the transfer-axis, $U_f(z^0) = U_i(z^0)$. Thus,

$$w_{ab} = \frac{2\pi}{\hbar q} \int dS \, |L_{a\gamma,b\delta}|^2 \left[\partial(U_f - U_i)/\partial z \big|_{z^0} \right]^{-1} \exp(-\beta U) \quad (30)$$

dS is an element of area on the reaction hypersurface. dS is a volume/in the internal coordinates for the reaction (again, see Marcus, ref. 1 for a concise definition of these quantities).

The notation is simplified by defining the frequency/tunnel factor K(R) as

$$K(R) = \frac{2\pi}{\hbar} |L_{a\gamma,b\delta}|^2 \left[\partial(U_f - U_i)/\partial z \big|_{z^0}\right]^{-1}.$$ (31)

Note, this quantity is not the same as κ which Marcus[1b] used. (Marcus[1] assumes κ is obtained by means of a Landau-Zener or equivalent form of analysis and is suitably averaged: the elementary frequency factor in Marcus's treatment continues to be k_BT/h, a quantity which follows automatically in the adiabatic limit-- see, the next section.) The transition probability is

$$w_{ab} = \frac{1}{q}\int dS \, K(R)\exp(-\beta U)$$ (32)

Following Marcus,[1b,2] we separate dS into dS'dR where R is the separation between sites a and b, as indicated. Thus,[1b]

$$\int_{S'} dS' \exp(-\beta U) = \exp(-\beta F^*(R))$$ (33)

(In this equation we have set Marcus's quantity ρ equal to unity,[1b] as Marcus suggests it should be.) In eqn (33), $F^*(R)$ is the configurational free energy of a system which has a potential energy U*:

$$e^{-\beta F^*(R)} = \int dV' e^{-\beta U^*}.$$ (34)

The rate constant for the transfer in the diabatic limit is

$$k = K(R)R^2 \exp(-\beta(w^r + \Delta F^*(R)))$$ (35)

(the reaction is assumed to be effectively bimolecular). The

configurational free energy for the reactants at infinite separation is

$$F^r = k_B T \ell n(q),$$ (36)

and

$$\Delta F^*(R) = F^*(R) - F^r(R)$$ (37)

where $F^r(R)$ is the configurational free energy of the system in its initial state prior to the transfer of the migrating species. w^r is the work required to prepare the system in an initial state with the sites for transfer, a and b, separated by a distance R. This work also includes the work required to form the site b (the vacancy) into which the transfer-species can migrate. This work is simply the difference between $F^*(h)$ and F^r.

It is clear that two quantities determine the size of the rate constant: the free energy of activation and the frequency/tunnel factor K(R) which depends directly on $L_{aa,b\delta}$. We have not yet specified the environmental subsystem in sufficient detail to be able to give numbers to the free energy of activation. Indeed, as there are so many ways to specify the environment of the reactive subsystem, it better at this point to leave the process unspecified. In the next section we consider the derivation of the rate constant in the adiabatic limit. The free energy of activation is the same quantity as found here. However, the method by which the configurational free energy for the transition state is to be found will be evident from that treatment.

The direct dependence of the rate constant for the transfer on the matrix elements for the tunnelling indicates that unless these quantities are non-vanishing, and indeed are of reasonable size, a tunnel-mechanism for the transfer is not reasonable. As the example we consider later shows, the distance over which the particle migrates in a tunnel-mechanism must be small, of the order of 0.5 to 1.0 Å.

Theory of the Activated Complex: adiabatic limit

As Marcus has stated,[1a] in order to develop the activated complex theory of reaction rates, one needs to assume (1) that some form of $(n-1)$-dimensional *hypersurface* of an n-dimensional hyper-space of the reacting system must be crossed; (2) that equilibrium statistical mechanics can be used to find the probability that the system is in any region of phase space on the reactant-side of the hypersurface; and (3), that the system crosses the hypersurface with unit probability and that reverse crossings can be neglected (adiabatic limit). Let $P(p,q)$ be the equilibrium density function in phase space:

$$P(p,q) = \exp(-\beta(H(p,q) - F)) \tag{38}$$

with

$$e^{-\beta F} = \frac{1}{h^n} \int d\Omega^{6n} \exp(-\beta H(p,q)). \tag{39}$$

H is the Hamilton function (the sum of the complete kinetic and

potential energies), p and q are $3n$-dimensional vectors for the momenta and coordinates of the particles of the system, and $d\Omega^{6n}$ is the volume element in phase space:

$$d\Omega^{6n} = \prod_{i=1}^{n} dp_i dq^i \tag{40}$$

where, as Marcus details,[1a] the sub- and superscripting of the indices denotes co- and contravariant vectors respectively.

The rate constant is defined by the integral:

$$k = \int d\Omega_r^{6n-1} \; \dot{q}_r P(p,q) \tag{41}$$

with

$$d\Omega_r^{6n-1} = \prod_{i=1}^{n} dp_i \prod_{i \neq r}^{n} dq^i \tag{42}$$

and q_r is that coordinate the constancy of which defines the hypersurface for the reaction (as Marcus notes, it is zero there). The integration of eqn (41) is carried out such that, in effect, only positive velocities ($\dot{q}_r$) of crossing are considered (negative velocities would account for a reverse crossing and the unrestricted sum of all forward and reverse crossings for all time would cancel to yield a trivial, null result). As a result, Marcus obtains[1a]

$$k = (k_B T/h) \exp(-\beta(F^{\ddagger} - F)) \tag{43}$$

with

$$e^{-\beta F^{\dagger}} = \frac{1}{h^{n-1}} \int_n \int_{i\neq r} dp_i dq^i \exp(-\beta H^{\dagger}(p,q)) \tag{44}$$

and $H^{\dagger}$ is the Hamilton function of the system which is constrained to exist on the hypersurface $q_r = 0$.

Marcus's analysis is general and to a significant degree abstract. Glyde[11] proceeded along similar lines of reasoning-- several years after Marcus--to obtain an expression for the rate of atomic self-diffusion in argon to a vacancy in an fcc lattice. Because Glyde chose a specific, regular (solid) system, his analysis could unfold in a particular manner; to be specific, Glyde was able to use a definite value of a specific coordinate to locate the position of the hypersurface. If $V(q)$ is the potential energy function for the system, and V_0 is the value of that function for the system in its initial state of equilibrium, Glyde obtains

$$k = |A|^{\frac{1}{2}} ((2\pi)^{3m+1}(k_B T)^{3m-1} m_1)^{-\frac{1}{2}} \exp(-\beta[V(a_0/2,\hat{r}) - V_0]) \tag{45}$$

in which $\frac{1}{2}a_0$ defines the location of the hypersurface with respect to a translation along a lattice coordinate; $\hat{r}$ is the collection of coordinates which remain to describe the system of m-species, and $|A|$ is the determinant of second derivatives of the potential V with respect to the coordinates, and finally, m_1 is the mass of the migrating particle. Glyde assumes, in evaluating the integral

$$\int dr_1 \ldots dr_m \, dr_1 \ldots dr_m \exp(-\beta H_{3m}(\dot{r},r)), \tag{46}$$

that the major contribution comes from terms which are near in value to the minimum value of V, V_0. Thus, the second order terms in a Taylor series (harmonic terms) contribute the most importantly to the integral--apart from the obvious contribution of V_0.

Glyde's approach,[11] together with Marcus's application of the general theory to the electron transfer,[1b] suggest the basis for constructing an algorithm to evaluate the rate constant in particular cases. Neither eqn (43) of Marcus's nor the eqn (45) of Glyde's is a final, usable expression for the rate constant until certain additional integrations have been performed. Marcus[1] indicates the incompleteness of eqn (43) by displaying the remaining integration, as shown by eqn (44). Glyde[11] notes the need for choosing values of $\hat{r}$ in $V(\frac{1}{2}a_0,\hat{r})$ such that V is a minimum in the region of the hypersurface (in the case of argon, the midpoint between the initial location of the atom and the vacancy, $\frac{1}{2}a_0$). Thus, Glyde considers the existence of one minimum in V and expands

$$V(\frac{1}{2}a_0,\hat{r}) = V^{\dagger}(\frac{1}{2}a_0,\hat{r}^{\dagger}) + \frac{1}{2}\sum A_{n,n'}^{\dagger} \delta r_n \delta r_{n'}, \tag{47}$$

to obtain

$$k = \frac{|A|^{\frac{1}{2}}_{3m}}{|A^{\dagger}|^{\frac{1}{2}}_{3m-1}} \frac{1}{2\pi m_1^{\frac{1}{2}}} \exp(-\beta(V^{\dagger} - V_0)). \tag{48}$$

A similar result was obtained by Marcus[1b] in his study of the electron-transfer reaction; the result was summarized in the last section.

At this point, Glyde evaluated k with the use of specific

Pair-wise additive potential energy functions. The migrating atom was moved a distance $\frac{1}{2}a_0$ to the midpoint of the transfer-distance and held there. The positions of the remaining neighbouring atoms were then adjusted to obtain a minimum value of the potential energy V. Moreover, because Glyde considered only a limited number of atoms, it was possible to evaluate all of the force constants in A and A^+. Altogether, Glyde's results, when compared with experiment, are impressively good.

Example: The evaluation of $L_{a0,b0}$ for a hypothetical ion-transfer

At this point we begin an examination of a simple, but representative system in order, first, to determine the matrix element $L_{a0,b0}$ for the transfer of an ion. In the next section we address the problem of evaluating the activation energy. The problem we consider is that of the diffusion of a lithium cation in a simple solvent. The solvent is assumed to be spherical with a polarizability a, but without any permanent dipole moment. The system is two-dimensional in order to make the physical aspects of the following analysis as transparent as possible; the restriction to two dimensions also ensures that no one should hold the results accountable to experiment. Thus, it is possible at this time to focus attention on the reasonableness of the system and its associated analysis. This simpler system ought to illustrate the way to apply the theory eventually to three-dimensional, real systems. Finally, in spite of the fact that the current view (for example, Wolynes[22]) regards ionic diffusion not to be an activated process, ionic diffusion is an example which readily

lends itself to analysis according to the theory as outlined in the preceeding paragraphs.

The evaluation of the matrix element $L_{a0,b0}$ (as indicated by the subscripts, a transfer between ground vibrational states) for the tunnel-transfer depends upon the definition of the reactive subsystem. For ion-transfer in a two-dimensional system, we consider the ion to be triangularly solvated (coordination number 3; for lithium, this generalizes simply to tetrahedral solvation in three dimensions). Diffusion takes place across one of the edges of the triangle of primary solvation. For simplicity, we assume that the centrally located ion is uniformly solvated in a regular, equilateral triangle of solvent. In addition, we include a regular distribution of molecules of secondary solvent such that three equivalent, potential vacancies exist across each of the three edges. This configuration is shown in Figure 1. The solvent which surrounds the reactive subsystem, as it has been defined here, is assumed to be randomly distributed; indeed, this can be accomplished relatively easily in computer simulation. The individual, random distributions of solvent will shift the position of mechanical equilibrium of the ion in its shell of primary solvent. However, with the use of a regular distribution of secondary solvent, the influence of the irregular, random distribution is minimized.

A vacancy is created by moving one of the molecules of solvent in the secondary layer an appropriate distance. The work which is required to do this is part of the overall energy of activation, but it is not directly part of the energy of reorganization for the solvent during the actual ion-transfer. We assume, for

simplicity, that the environment about the ion in its initial and final locations is mechanically the same. The transfer-axis is defined to pass through the positions of mechanical equilibrium which have been found for the ion in its reactive subsystem. Upon placing the reactive subsystem into the remainder of the solvent, there will be adjustments to many of the parameters. These adjustments amount to self energies of interaction between the ion and its primary (and secondary) shell of solvent and the bulk of the system.

The potential energy function for the interaction between the ion and one of the molecules of solvent is taken to be

$$V(r) = - Z_i \alpha e^2 \frac{1}{2r^4} + \frac{B}{r^{12}} \qquad (49)$$

in which α is the polarizability of the solvent, Z_i is the charge on the ion and B is a constant which is associated with the repulsion. [The "more popular" exponential form for the repulsion could have been used. However, the symmetry-adapted form of the Taylor series is more complicated in that case. The complication does not seem to be warranted at this stage in the development.] The symmetry-adapted Taylor series for eqn (49) is

$$V(\underline{r}+\underline{R}) = - \sum_{n=0}^{\infty} \sum_{l=0}^{n} \frac{A_{nl}}{n!} P_l(\hat{r}\cdot\hat{R})(-r_</r_>)^n \left[\frac{Z_i \alpha e^2}{4r_>^4}(n-l+1)!!(n+l+2)!! \right.$$
$$\left. - \frac{B}{10!r_>^{12}}(n-l+9)!!(n+l+10)!! \right] \qquad (50)$$

in which, as before, $r_{<(>)}$ is the lesser (greater) of r and R.

The vectors $\underline{r}$ and $\underline{R}$ are drawn in the same sense as earlier, eqn (2).

The complete potential energy function for the interaction of the ion with its surrounding solvent is the sum of individual terms of the form of eqn (50); thus, V(z) is given by eqn (1) with the restriction to the z-axis indicated by eqn (4) and (5).

The analysis which leads to an explicit formula for $L_{a0,b0}$ makes use of the ground state harmonic oscillator wavefunctions in one dimension:

$$\phi_i(z_i) = (a_i/\pi)^{\frac{1}{4}}\exp(-\tfrac{1}{2}a_i z_i^2) \qquad i = (a,b) \qquad (51)$$

for the ion located at site a or site b. In the following discussion, where confusion is not likely to arise, the exponential coefficient a_i is replaced by the site label: $a_a = a$ and $a_b = b$. We now find that it is possible to make an additional simplification of the potential energy function. The integrals which involve the potential can be expressed in the general form

$$I_n = \frac{2}{R^{n+q}}\int_0^R dz\, z^n f(z) + 2R^n\int_R^{\infty} dz\, z^{-n-q} f(z) \qquad (52)$$

in which q represents a collection of constants (including l, cf., eqn (50)). n is the index of the Taylor expansion and f(z) is an even function which arises from the product of harmonic oscillator wavefunctions. We find in general that the scaling to dimensionless units, together with the value of R which is involved, allows us to reduce the pair of integrals (52) to

$$I_n = \frac{1}{R^{n+q}} \int_{-\infty}^{\infty} dz\; z^n f(z) \tag{53}$$

in which the limit of integration in the first integral of (52) has been extended to infinity. The specific evaluation of the second integral in eqn (52) (generally) yields vanishing results. Thus, the first integral (which defines the incomplete gamma functions and is thereby related to the error integral) is essentially the same as eqn (53).

We now write the potential energy function as

$$V(z) = \sum_{n=0}^{\infty} C(|R|,n)(-z)^n \tag{54}$$

for which (R) is the set of distances from the origin to the various source molecules. For one molecular source at R,

$$C(R,n) = -\frac{1}{R^n} \sum_{\ell=0}^{n} \frac{A_{n\ell}}{n!} P_\ell(\cos\theta_R) \left\{ \frac{Z_i \alpha e^2}{4R^4}(n-\ell+1)!!(n+\ell+2)!! \right. \\ \left. -\frac{B}{10|R|^{12}}(n-\ell+9)!!(n+\ell+10)!! \right\} \tag{55}$$

From Figure 1, it is clear that a useful origin of coordinates is located on the transfer-axis at the edge of the primary triangle of solvent. This edge borders the vacancy into which the ion migrates. In general, one can establish the origin of coordinates at the location of the maximum value of the potential energy barrier. Thus, with the location of sites a and b on the z-axis as Z_a and Z_b, we can write

$$z_a = z - Z_a$$
$$z_b = z + Z_b. \tag{56}$$

The various individual matrix elements in $L_{a0,b0}$ can now be evaluated.

For a two-level system (which here is a degenerate two-site system), the matrix element $L_{a0,b0}$ can be expressed as

$$L_{a0,b0} = \frac{1}{1 - S_{ab}^2}(V_{ab}^b - S_{ab} V_{bb}^b) \tag{57}$$

and now, specifically,

$$V_{ab}^b = \langle a0|V(z)|b0\rangle + \langle a0|H_{env}|b0\rangle - \tfrac{1}{2}k_b\langle a0|z_b^2|b0\rangle \tag{58}$$

$$V_{bb}^b = \langle b0|V(z)|b0\rangle + \langle b0|H_{env}|b0\rangle - \tfrac{1}{2}k_b\langle b0|z_b^2|b0\rangle. \tag{59}$$

The non-diagonal matrix elements of the operators $\tfrac{1}{2}k_a z_a$ and $\tfrac{1}{2}k_b z_b$ are

$$\tfrac{1}{2}k_j^2\langle 10|z_j^2|10\rangle = \frac{k_1}{\sqrt{2}}\frac{(ab)^{\frac{1}{2}}}{(a+b)^{3/2}}\exp\left(-\frac{ab}{2(a+b)}R_{ab}^2\right)\left[1 + \frac{a_1 Z_1^2}{a+b}\right]. \tag{60}$$

When a = b and $Z_a = Z_b = Z$,

$$\lim_{a\to b}\langle 10|z_j^2|10\rangle = \frac{1}{4a}(2 + aZ^2)\exp(-aZ^2). \tag{61}$$

The various matrix elements of the operator V(z) are now found. Because of the location of the origin of coordinates, the diagonal elements are not the straightforward matrix elements of z^n when evaluated with reference to one centre. Instead, one finds

$$\langle b0|V(z)|b0\rangle = \sum_{n=0}^{\infty} C((R),n)(-1)^n \langle b0|z^n|b0\rangle \quad (62)$$

and a similar term for $\langle a0|V(z)|a0\rangle$. The specific form of the matrix element $\langle b0|z^n|b0\rangle$ is

$$\langle b0|z^n|b0\rangle = \sum_{\substack{m=0 \\ (even)}}^{n} \binom{n}{m} z_b^{n-m} \frac{(m-1)!!}{(2b)^{m/2}} \quad (63)$$

in which $\binom{n}{m}$ is the binomial coefficient. The non-diagonal matrix element of z^n is

$$\langle a0|z^n|b0\rangle = \sqrt{Z}\,\frac{(ab)^k}{(a+b)^{\frac{3}{2}}} \exp\left[-\frac{ab}{2(a+b)}R_{ab}^2\right]$$
$$\times \sum_{\substack{m=0 \\ (even)}}^{n} \binom{n}{m} \frac{(aZ_a - bZ_b)^m}{(a+b)^{(n+m)/2}}(n-m-1)!!. \quad (64)$$

The matrix elements of the environmental operator H_{env} can be examined in the following way. According to the definition of H_{env}, it consists in part of those terms in the solute-solvent interaction which were omitted when defining the reactive subsystem; thus, H_{env} is a sum of a (large) number of additional ion-solvent interactions. There are of course also contributions from the momenta of these remaining molecules of solvent, but we assume that the local wavefunctions have an extremely weak dependence on these additional coordinates. As a result, in the matrix elements

$\langle 10|H_{env}|10\rangle$ the ion-solvent interactions dominate.

For any molecule of solvent, we assume that outside of the primary (and perhaps secondary) shell of solvation, there is an effective potential energy function $v_{eff}(r)$ [which we assume here has the same form as eqn (49)]. In the spirit of the method suggested by Sinanoğlu[23,24] the matrix element of H_{env} is written as

$$\langle 10|H_{env}|10\rangle = \left\{\sum_{n=0}^{N_t} P_n^2/2M_n + \sum_{m>n} U_{m,n}\right\} S_{i,j}$$
$$+ \rho \int d^3r \langle 10|v_{eff}(z+r)|10\rangle g^{(2)}(r) \quad (65)$$

where N_t is the total number of environmental species outside of the transfer-species, and $U_{m,n}$ is the solvent-solvent interaction. $v_{eff}(z+r)$ is expanded about the equilibrium position of the ion on the transfer axis according to eqn (50). In eqn (65), ρ is the number density of the solvent. Because the radial distribution $g^{(2)}(r)$ is a scalar quantity, only the $l=0$ contributions survive in the integration over the Taylor series. If, following Halicioğlu and Sinanoğlu,[24] we write

$$g^{(2)}(r) = 0 \quad \text{for} \quad r < R'$$
$$= 1 \quad \text{for} \quad r \geq R' \quad (66)$$

where here R' is the sum of the solute and solvent radii, then

$$\rho \int d^3r \langle 10|v_{eff}(z+r)|10\rangle g^{(2)}(r) =$$

$$- \rho(R')^3 \sum_{n=0}^{\infty} \frac{1}{(n+1)!} T \langle 10|(-z)^n|10\rangle \frac{1}{(R')^n} \left[\frac{Z_1 a' e^2}{4(R')^4} (n+2)! \right.$$
$$\left. - \frac{B}{10!(R')^{12}} (n+10)! \right]. \quad (67)$$

The matrix elements of z^n are the same as used previously. In order to consider some limiting forms of $L_{a0,b0}$, eqn (57) is regrouped as

$$L_{a0,b0} = \frac{1}{1 - S_{ab}^2} \left(\langle a0|V(z)|b0\rangle - S_{ab}\langle b0|V(z)|b0\rangle \right.$$
$$+ \langle a0|H_{env}|b0\rangle - S_{ab}\langle b0|H_{env}|b0\rangle + \tfrac{1}{2}k_b \left(\langle a0|z_b^2|b0\rangle \right.$$
$$\left. - S_{ab}\langle b0|z_b^2|b0\rangle \right) \Big) \quad (68)$$

The first two groupings of terms in V(z) and H_{env} can be treated in the same way. Write

$$\langle a0|V(z)|b0\rangle - S_{ab}\langle b0|V(z)|b0\rangle = \exp\left[- \frac{ab}{2(a+b)}R_{ab}^2\right]$$
$$\times \sum_{n=0}^{\infty} C((R),n) \sum_{m=0}^{n} \left[\frac{\sqrt{2}(ab)^{\frac{1}{2}}}{(a+b)} \, \frac{1}{(n+m+1)/2} (aZ_a - bZ_b)^m \right.$$
$$\left. - \frac{z_b^m}{(2b)^{(n-m)/2}} (n-m-1)!! \right]. \quad (69)$$

When a = b and $Z_a = Z_b = Z$, eqn (69) reduces to

$$\langle a0|V(z)|b0\rangle - S_{ab}\langle b0|V(z)|b0\rangle = - \exp(-aZ^2) \sum_{n=2}^{\infty} C((R),n)$$
$$\times \sum_{m=2}^{n} 2^{(m-n)/2} (\sqrt{a}Z)^m (n-m-1)!! \quad (70)$$

The limiting form for the environmental factor, H_{env}, reduces as follows:

$$\langle a0|H_{env}|b0\rangle - S_{ab}\langle b0|H_{env}|b0\rangle = \langle a0|v_{eff}|b0\rangle - S_{ab}\langle b0|v_{eff}|b0\rangle \quad (71)$$

As v_{eff} is of the same form as V(z), the limiting form is similar to eqn (70). It differs only in the definition of C((R),n). The third set of terms which depend upon matrix elements of z_b yields

$$\tfrac{1}{2}k_b (\langle a0|z_b^2|b0\rangle - S_{ab}\langle b0|z_b^2|b0\rangle) = \tfrac{1}{4}\hbar\omega_b \exp\left[- \frac{ab}{2(a+b)}R_{ab}^2\right]$$
$$\times \left[\left[1 + \frac{(bZ_b)^2}{a+b} \right] \sqrt{2} \, \frac{(ab)^{\frac{1}{2}}}{(a+b)^{3/2}} - \frac{1}{2b} \right]. \quad (72)$$

In the limit as a = b and $Z_a = Z_b = Z$, we find

$$\tfrac{1}{2}k_b (\langle a0|z_b^2|b0\rangle - S_{ab}\langle b0|z_b^2|b0\rangle) = \frac{1}{8} aZ^2\hbar\omega_b \exp(-aZ^2). \quad (73)$$

Example: The activation energy for the hypothetical transfer

The activation energy for the species-transfer from one state to another is influenced by a number of obvious quantities. As was indicated earlier, the reactive subsystem is defined in the absence of much of the remainder of the system; in order to define the mechanics of the transfer-species, one needs only to consider the interaction between the mobile species and its surroundings of nearest neighbour, rigidly held solvent. The relaxation of the notion of the rigidity of the field of solvent is discussed shortly in the context of optimal configurations and in terms of Monte Carlo techniques. The activation energy, on the other hand, is determined by the interactions already mentioned, and all others. Thus, for example, one can consider the work needed to form a configuration from which the transfer can take place. Further activation will require additional distortion of the system; the amount of this additional distortion which is needed is determined by optimizing the total energy of the system in the transition state.

In the following considerations, we define the *transfer-point* to be that location on the transfer-axis at which the energy of the system is a maximum. This maximal energy is determined for the system in its initial configuration of solvent. Only the transfer-species has been displaced.

The simple two-dimensional system which is illustrated by Figure 1 demonstrates features of the transition state which contribute to the activation energy and which influence the

choice of adiabatic versus diabatic limits for the reaction. The reactive system of Figure 1, for example, is originally a rhombohedron. For simplicity, assume that the locations of the sources on the long diagonal axis remain fixed. As Table 1 indicates, as the rhombohedron stretches along the short diagonal axis to assume a square planar shape, the location of the position of equilibrium of the ion on the long axis tends toward the centre of the (forming) square. There appear to be significang distortions of the environment which can adiabatically carry the transfer-species along through the transition-point on the transfer-axis.

Given a configuration of solvent which is distributed about an ion, and given a neighbouring vacancy, the following can occur. First, when the ion is placed at the location of the maximum of the energy-barrier on the transfer-axis, and the system is allowed to relax to the lowest possible energy for the ion at that location, a position of stable mechanical equilibrium will be found for the migrating particle. In this case, the transition state can be reached *via* an adiabatic transfer of the particle from its initial position. The tunnel factors will be close to unity.

On the other hand, when the ion is placed at the location of the maximum of the energy-barrier on the transfer-axis, and the system is allowed to relax to the lowest possible energy for the ion at that location, a position of unstable mechanical equilibrium will be found for the migrating particle. In this case, the ion can tunnel from an initial state which is physically removed from the energy-barrier at the transfer point. One assumes that the energy of activation for this type of transfer involves

a minimum of adjustment of the solvent; the (more energetic) motions of the whole molecules do not occur. Such a transfer conforms to the diabatic limit. In the diabatic limit, the tunnel factors for the transition are calculated with respect to the initial state configuration (which includes the vacancy), but the activation energy is calculated with respect to the transfer-species at the location of the transition-point.

At this point, we assert that for an adiabatic transfer of a *heavy-centre, it is necessary for the heavy-centre to follow a moving position of mechanical equilibrium; the moving position of equilibrium takes the heavy-centre from its initial state through the transition state to its final state. The position of local mechanical equilibrium moves by virtue of the migrating nature of the fluctuations in the environment of the solvent.* Thus, we also assert the corollary that at any point along the trajectory which the heavy-centre follows, the value of the second derivative of the potential energy function with respect to the reaction coordinate *must* be positive definite.

This statement concerning the nature of the mechanics of the migration of the heavy-centre is in accord with the usual formula-tion of an ideal, reversible transformation in thermodynamics. Thus, if one fixes the position of the migrating particle at a location on the transfer-axis which corresponds to the location of the transition state, and if this position locates a *saddle point* with respect to the complete potential energy function for the (many-dimensional) system, then any optimization which yields the *minimum* energy of the system at that point must yield a complete set of second derivatives (evaluated at the saddle point) in eqn (47) which

in turn yields a positive definite symmetric matrix. Optimization (*viz.*, the search for the minimum in the total energy) at the transition state involves all coordinates *except* the coordinate which defines the transfer-axis (the reaction coordinate). Our assertion that the migrating species must also occupy a state of local mechanical equilibrium (for an adiabatic transfer) with respect to any displacement along the transfer-axis at the saddle point which locates the transition state is an additional condition. This additional condition can be used (a) to hasten convergence to the optimal, minimum energy of the transition state, and (b) as a test of the validity of any transition state which one chooses to define.

Because of the introduction of the condition of equilibrium with respect to the transfer-axis at the transition state, and the constraint of holding the system at that point during the process of minimizing the total energy, the energy defined for the system under these conditions is a legitimate thermodynamic free energy. The artificial constraint of holding the transferring species at a physical location which one believes to be the location of the transition state is in no sense different from any other physical boundary which one introduces in any system in order to determine the thermodynamic quantities for the system in a state of equilibrium. The release of the constraint obviously defines a system in a non-equilibrium state from which relaxation to another state of equilibrium is ensured.

It is generally acknowledged that for the transition state theory it is necessary to calculate the work which is required to prepare the initial state from which the ultimate transfer takes

place. However, except for some simple cases, few algorithms exist to carry out this task. In view of the assertions made above concerning the mechanical distinction between the diabatic and adiabatic limits for transfer, we propose the following conditions to use to determine the work to prepare the initial state in the reactive system.

To begin, for either the diabatic or adiabatic transfer, it is necessary that there be well-defined mechanical initial and final states; this holds for all types of species-transfer, including electron transfer. Thus, it is necessary in most instances of heavy-centre transfer that a vacancy or some form of acceptor-structure be created into which the transferring species can migrate. Part of the work to prepare the initial state for the transfer, therefore, is the work which is needed to form a receptor-structure (a vacancy) which neighbours the initial location of the migrating species.

We now assert that if the transfer is *wholly adiabatic*, the migrating species moves from its initial position to the transition state *via* a sequence of (reversible) adiabatic steps. For the adiabatic transfer, the only work-term which needs to be calculated is the work to form the vacancy. The migrating particle moves to the transition state; the transition state is determined algorithmically with the methods of optimization which have been discussed above.

If the transfer is diabatic, the work to form the vacancy into which the particle moves needs to be supplemented with the work which is required to move the transfer-species to an optimal init. 1 state from which tunnelling to the final state can take

place. This optimal initial state is determined by moving the transfer-species adiabatically along the transfer-axis; for each infinitesimal advance of the transfer-species, the energy of the entire system is optimized. The particle moves forward toward the transfer-point until one finds that (after optimization of the system-energy) the particle is in a state of *unstable* mechanical equilibrium. The particle is then removed to the last position for which *stable* mechanical equilibrium was found. This limiting position (prior to reaching the transition state) defines the initial state for the diabatic transfer. From this point, the particle usually tunnels to the final state through the remaining barrier of the system.

In summary, we contend that there is an adiabatic component to every transfer. If the adiabatic transfer takes the particle to a state of stable mechanical equilibrium in the transition state, then the entire transfer is adiabatic. If, on the other hand, a limiting position is reached prior to the transition state, and if this limiting position is the last position for which the particle can remain in a state of stable mechanical equilibrium with respect to the entire system (which has been optimized in energy), then this last, limiting position defines the initial state for the diabatic transfer.

In view of these assertions, therefore, it is neither reasonable nor consistent simply to estimate (*via* a crude Boltzmann-type of weighting) a fraction of particles which are in some (pre-ordained) arbitrary configuration when that configuration has not been determined according to the prescription set out above. The consequence of choosing any arbitrary configuration is simply that

one is likely, more often than not, to choose a configuration from which tunnelling is the only route for the transfer; and, when the tunnel-factors are calculated, one finds that the transfer is not likely to occur. The calculated tunnel-factors for the model system, which are discussed in the next section, support this conclusion.

Numerical estimates of the tunnel-factors for the hypothetical transfer

The general form of the pair-wise interaction which operates between the ion and the surrounding solvent is given by eqn (49). In order to use this quantity, it is necessary to assign values to the parameters α (the polarizability of the solvent) and B (for the repulsion). Because the far infrared-active spectrum of solvated lithium has been thoroughly examined,[7-10] we use lithium in the example. As a consequence, we consider the (planar) vibration to be in the range of 430 cm^{-1}. This frequency is used to determine a force constant. For a solvent of molecular weight of about 50 amu, and a basic coordination of three, the force constant is estimated to be 73,000 dyn cm^{-1}.

The ion which is enclosed in a planar configuration of solvent has an associated force constant of

$$k = -\frac{3}{R^6}(Z\alpha e^2 - 44B/R^8) \qquad (74)$$

in which R is the equilibrium distance between the ion and the solvent which is located at the vertex of the (regular, equilateral)

triangle of solvation. The condition of equilibrium which operates for each ion-solvent pair is

$$6B/R^8 = Z\alpha e^2. \qquad (75)$$

Thus, the expression for the force constant reduces to

$$k = 144 \frac{B}{R^{14}}. \qquad (76)$$

Assume that the ion-solvent radius R is 3 Å (measured from the centre of the ion to the centre-of-gravity of the solvent). With k = 73,000 dyn cm^{-1}, we find α = 9.62 Å^3 and B = 2.43×10^{-7} erg Å^{12}. Table 1a shows the change in the location of the position of equilibrium for the ion on the (original) long diagonal axis of the rhombohedron of solvent. As the median axis expands, the ion moves closer to that axis along the long axis. However, with the original location of the solvent on the transfer-axis, even for an extreme expansion (such that the median ion-solvent radius exceeds the equilibrium value of 3 Å), the ion does not move to a position of equilibrium at the centre-of-gravity of the collection of (four) molecules of solvent.

It is possible for the ion to assume a central position of stable mechanical equilibrium if the axial molecules of solvent move in toward the centre of the structure. Such a situation is indicated in Table 1b. In this case, the axial molecules are located a distance of 3 Å from the centre of the entire structure. As the table indicates, a compression of the median molecules of solvent eventually results in the establishment of the centre-

of-gravity as the position of stable mechanical equilibrium. This position also would correspond to the location of the transition state. Thus, such a transition would be adiabatic.

For the possible positons of (initial state) equilibrium for the transfer-species as shown in Table 1a, one finds immediately that the tunnel-factors for the transfer in the diabatic limit vanish. The reason for the vanishing of tunnelling, of course, is the vanishing of the vibrational overlap between the initial and final states. This is in accord with the conclusion reached earlier.

On the other hand, for the potential energy function illustrated in Tables 1a and 1b, it is clear that in the case of a compression of the system, it is possible for tunnelling to occur whenever the separation between the initial and final states is a reasonably small value.

In assuming a value of $R = 3$ Å, we can account for the vibrational frequency. As has been shown elsewhere,[9,10] the values of the polarizability for the solvent and other quantities are in agreement with measured, macroscopic values. However, as the smallness of the tunnel-factors indicates in Table 1a, the choice of the centre-of-gravity of the solvent is not necessarily realistic (unless, perhaps, one is examining a reaction in the adiabatic limit or, as Table 1b suggests, a significant distortion takes place to prepare a suitable initial state). As a number of studies of discrete solvation have shown,[25,26] the consideration of specific ion/solvent-atom and ion/solvent-bond charge and repulsive interactions leads to accurate estimates of a number of the tunnel-factors; and, these estimates do show evidence that tunnelling

would lead to reasonable rates.

Assume the same value for the force constant, 73,000 dyn cm^{-1}.

Now assume that the ion interacts the most strongly with an atom of the solvent which is 1 Å away. With $R = 1$ Å, we find $\alpha = 0.0139$ Å^3 and $B = 5.1 \times 10^{-14}$ erg Å^{12}. The behaviour of the system which is predicted with the use of these parameters is indicated in Table 1c. In this case, tunnelling is seen to be possible. Moreover, we find that the intrinsic barrier heights (omitting considera- tion of the role of solvent, at this point) are small.

Discussion

The emphasis in this paper has been to develop a theory of the heavy-centre transfer in the diabatic limit. In order to do so, we have argued that it is possible to construct a Born-Oppenheimer-Holstein type of separation in order to isolate the dynamics of the transfer-species from those of the remainder of the system. Such a separation would seem to imply a weak coupling limit for the interaction between the transfer-species and its environment; indeed, this can be the case. However, as we have also argued, the diabatic limit can apply to those cases for which (through mechanical considerations) it is impossible for the system adiabatically to transfer the migrating species to the transition state. The system does prepare an "initial state" (through fluctuations) from which the transfer to the final state takes place *via* tunnelling through the remaining barrier. This initial state is as close to the transition state as the system can accomodate by an adiabatic transformation; the condition, as

indicated earlier in the paper, is that the particle should occupy a state of stable, mechanical equilibrium in this initial state. For the cases for which it is impossible for an adiabatic transfer to take place to the transition state, it is possible to carry out a Born-Oppenheimer-Holstein separation even though (effectively) the interactions between the transfer-species and its environment may be strong. The separation is carried out in the sense that the initial state consists of a "frozen" environment within which the transfer-species must tunnel from one location to another.

In this frozen environment, as indicated, the mechanics of the transfer-species are determined. A rate constant for the passage in the diabatic limit can be calculated for an *ensemble* of such systems. In this sense, the rate constant is determined with the use of Monte Carlo methods of averaging. One considers the random generation of a collection of configurations of solvent. Each configuration can be weighted in the manner of the Metropolis sampling technique.[27] The collection of rate constants is then directly averaged as in the usual form of Monte Carlo calculations.

On the other hand, as we have emphasized here, it appears possible to seek optimal configurations of the environment about the transfer-species. Rate constants are then calculated for these single or few configurations. As the configurations are optimal, the values for the rate constants should agree with the experimental values. This indeed has been found to be the case by Glyde[11] in a study of the self-diffusion of argon.

We believe that in this note we have suggested new algorithmic approaches to the evaluation of theoretical rate constants for heavy-centre transfers which take place in condensed phases.

We noted a distinction between two types of transfer: a long-distance and a short-distance transfer. We noted further that the long-distance transfer is usually an adiabatic type of transfer. Transfers over relatively short distances may often fall in the diabatic limit, although this need not be the case. In order to consider the transfer in the short-distanced, diabatic limit, we have shown that the use of a symmetry-adapted expansion of the collection of pair-wise potential energy functions for the inter-action of the transfer-species with its surroundings can lead easily to values for the tunnel-factors which must be calculated. In addition, the general considerations of the problem of the evaluation of the energy of the transition state have led to suggestions for the determination of that quantity for model systems. In particular, the condition of stable mechanical equilibrium for the transfer-species in the transition state would seem to be a useful condition to use to distinguish between reactions in the adiabatic and diabatic limits. In subsequent papers the general ideas tenatively explored here shall be applied to specific systems.

Appendix

We have shown elsewhere[15] that the symmetry-adapted form of the Taylor series can be expressed in general as

$$G(\underline{r}+\underline{R}) = (4\pi)^{3/2} \sum_{n,L,M,\ell,m} \frac{r^n}{n!} A_{n\ell} Y_{LM}(\hat{R}) Y_{\ell m}(\hat{r})$$

$$\times \left[\frac{2L+1}{(2\ell+1)(2\lambda+1)} \right]^{\frac{1}{2}} (L\ell 00|\lambda 0)(L\ell Mm|\lambda \mu) I_{nL}(R) \qquad (A1)$$

where $A_{n\ell}$ is given by eqn (3), $(L\ell Mm|\lambda\mu)$ is the Clebsch-Gordan coefficient and $I_{nL}(R)$ is

$$I_{nL}(R) = \frac{1}{(2\pi)^3} \int_0^\infty dk \, k^{n+2} f(k) j_L(kR) \qquad (A2)$$

in which $f(k)$ is the radial transform of $F(r)$ in

$$G(r) = Y_{\lambda\mu}(\hat{r}) F(r) \qquad (A3)$$

and $j_L(kR)$ is the spherical Bessel function of the first kind.[17]

In the limit of a scalar function $G(r)$, $\lambda=\mu=0$. An individual term in the Taylor series is

$$\frac{1}{n!}(\underline{r}\cdot\nabla)^n G(r) = \sqrt{4\pi} \, \frac{r^n}{n!} \sum_\ell (-1)^{n+\ell} A_{n\ell} P_\ell(\hat{r}\cdot\hat{R}) I_{n\ell}(R) \qquad (A4)$$

From eqn (A2) we can write

$$(2\pi)^3 I_{n\ell}(r) = \int_0^\infty dk \, k^{n+2} f(k) j_\ell(kr)$$

$$= 4\pi^{5/2}(-1)^{(n+\ell)/2} r^\ell \left[\frac{d}{rdr} \right]^\ell \frac{1}{r}(d/dr)^{n-\ell} rF(r) \qquad (A5)$$

Following Todd, Kay and Silverstone,[28] we can show that

$$r^\ell \left[\frac{d}{rdr} \right]^\ell r^{-1}(d/dr)^{n-\ell} rF(r) = \sum_{q=0}^{\ell} \frac{(-1)^q(\ell+q)!}{(\ell-q)!\Gamma(2q)!!} \, r^{-q} \left(\frac{n-q}{r} + \frac{d}{dr} \right)$$

$$\times (d/dr)^{n-q-1} F(r). \qquad (A6)$$

Thus,

$$I_{n\ell}(r) = \frac{1}{\sqrt{4\pi}}(-1)^{(n+\ell)/2} \sum_{q=0}^{\ell} \frac{(-1)^q(\ell+q)!}{(\ell-q)!\Gamma(2q)!!} \, r^{-q} \left(\frac{n-q}{r} + \frac{d}{dr} \right)$$

$$\times (d/dr)^{n-q-1} F(r). \qquad (A7)$$

Table 1a: Potential: $R = 3$ Å, $\alpha = 9.62$ Å^3, $\beta = 2.42 \times 10^{-7}$ erg Å^{12}.

R_e	z_0	E_{min}
2.1	1.79	1.06
2.2	1.73	0.50
2.3	1.68	0.62
2.4	1.62	-0.28
.		
3.1	1.17	-1.02
3.2	1.11	-0.99
3.3	1.08	-0.97
3.4	1.06	-0.94
.		
4.1	1.12	-0.70
4.2	1.13	-0.67
4.3	1.14	-0.65
4.4	1.15	-0.63

Table 1b: Potential: $R = 2$ Å, $\alpha = 9.62$ Å^3, $\beta = 2.42 \times 10^{-7}$ erg Å^{12}

R_e	z_0	E_{min}	L_{ab}	S_{ab}
2.0	0.80	59.70	4.22×10^{-19}	8.9×10^{-24}
2.1	0.71	39.23	8.3×10^{-15}	6.9×10^{-19}
2.2	0.61	25.12	1.3×10^{-10}	4.0×10^{-14}
2.3	0.49	15.51	1.9×10^{-6}	2.3×10^{-9}
2.4	0.35	9.08	7.5×10^{-3}	3.9×10^{-5}
2.5	0.12	4.84	3.8	0.3
2.6	0.00	...	...	...
2.7	0.00	...	...	...

Table 1c: Potential: $R = 1$ Å, $\alpha = 0.0132$ Å^3, $\beta = 5.1 \times 10^{-14}$ erg Å^{12}

R_e	z_0	E_{min}	L_{ab}	S_{ab}
0.70	0.60	0.118	3.5×10^{-7}	1.1×10^{-13}
0.80	0.54	-0.031	7.9×10^{-7}	3.1×10^{-11}
0.90	0.48	-0.096	-5.6×10^{-5}	5.0×10^{-9}
1.00	0.41	-0.113	-3.4×10^{-3}	8.8×10^{-7}
1.10	0.36	-0.108	-3.4×10^{-2}	2.2×10^{-5}
1.20	0.35	-0.096	-5.1×10^{-2}	3.9×10^{-5}

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References

1. (a) R. A. Marcus, J. Chem. Phys., 1964, $\underline{41}$, 2624; (b) J. Chem.
   Phys., 1965, $\underline{43}$, 679

2. P. P. Schmidt, J. Chem. Phys., 1973, $\underline{58}$, 4384

3. R. A. Marcus, Ann. Rev. Phys. Chem., 1964, $\underline{15}$, 155

4. R. R. Dogonadze, in *Reactions of Molecules at Electrodes*, N. S.
   Hush, ed. (J. Wiley & Sons, NY, 1970)

5. P. P. Schmidt, SPR Electrochemistry, 1975, $\underline{5}$, 21; 1978, $\underline{6}$, 128

6. F. Basolo and R. G. Pearson, *Inorganic Reactions, A study of
   metal complexes in solution* (J. Wiley & Sons, NY, 2nd Ed., 1967);
   see also, J. Hine, Adv. Phys. Organic Chem., 1977, $\underline{15}$, 1

7. W. F. Edgell, J. Lyford, R. Wright, W. Risen and A. Watts, J.
   Amer. Chem. Soc., 1970, $\underline{92}$, 1493

8. B. W. Maxey and A. I. Popov, J. Amer. Chem. Soc., 1969, $\underline{91}$, 20

9. P. P. Schmidt, B. S. Pons and J. M. McKinley, J. Chem. Soc.
   Faraday 2, 1980, $\underline{76}$, 979

10. P. P. Schmidt, J. Chem. Soc. Faraday 2, 1982, $\underline{78}$, 123

11. H. R. Glyde, Rev. Mod. Phys., 1967, $\underline{39}$, 373

12. A. H. Opie, Phys. Rev., 1968, $\underline{172}$, 640

13. I. R. Senitzky, Phys. Rev., 1961, $\underline{119}$, 670; $\underline{124}$, 642

14. A. Nitzan and J. Jortner, Mol. Phys., 1973, $\underline{23}$, 713

15. J. M. McKinley and P. P. Schmidt, J. Chem. Soc. Faraday 2,
    1982, $\underline{78}$, 867

16. G. Arfken, *Mathematical Methods for Physicists* (Academic Press,
    New York, 2nd edn, 1970)

17. M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley

-53-

    & Sons, New York, 1957)

18. T. Holstein, Ann. Phys. (N.Y.), 1959, $\underline{8}$, 343

19. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*
    (Oxford University Press, London, 1954)

20. R. A. Marcus, J. Chem. Phys., 1964, $\underline{41}$, 603

21. R. A. Marcus, J. Chem. Phys., 1964, $\underline{41}$, 610

22. P. G.Wolynes, Ann. Rev. Phys. Chem., 1980, $\underline{31}$, 345

23. O. Sinanoğlu, Chem. Phys. Letters, 1967, $\underline{1}$, 340

24. T. Halicioğlu and O. Sinanoğlu, Ann. N. Y. Acad. Sci., 1969,
    $\underline{158}$, 308

25. J. Sunner and P. Kebarle, J. Phys. Chem., 1981, $\underline{85}$, 327

26. I. Eliezer and P. Krindel, J. Chem. Phys., 1972, $\underline{57}$, 1884

27. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller,
    and E. Teller, J. Chem. Phys., 1953, $\underline{21}$, 1087

28. H. D. Todd, K. G. Kay and H. J. Silverstone, J. Chem. Phys.,
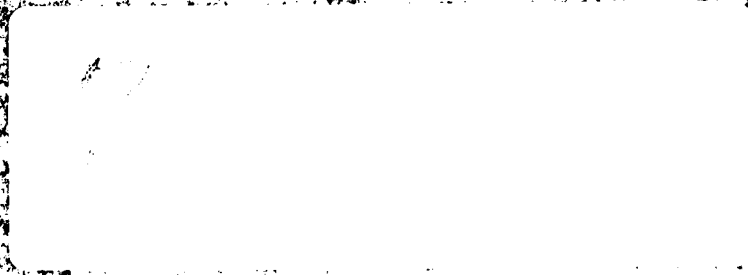   1970, $\underline{53}$, 3951

Figure Caption

Figure 1. The arrangement of solvent (labelled S) and transferrable
ion (Li) in the two-dimensional, model system. The coordination
is three-fold, planar. The transfer-axis is the z-axis, the
median, short axis of the rhombohedron of the reactive subsystem
is labelled y. The initial state is a, the final state is b.

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